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(71) Applicant *(for all designated States except US)*: OY ALKO AB [FI/FI]; Box 350, SF-00101 Helsinki (FI).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : LEPPÄNEN, Olavi [FI/FI]; LAAKSO, Raimo [FI/FI]; Oy Alko Ab, Box 350, SF-00101 Helsinki (FI).

(74) Agent: PAPULA REIN LAHTELA OY; Box 981, Kansakoulukatu 5 A, SF-00101 Helsinki (FI).

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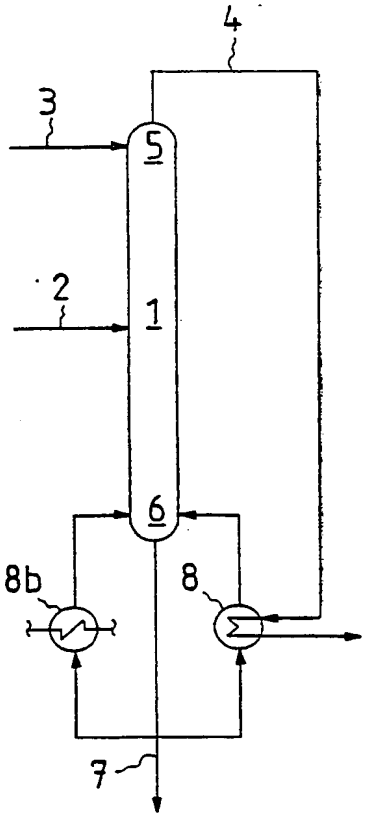
(54) Title: METHOD AND APPARATUS FOR THE PURIFICATION OF A TWO-COMPONENT LIQUID MIXTURE BY DISTILLATION

(57) Abstract

Method for the purification of a two-component liquid mixture by distillation, whereby the liquid mixture to be purified is fed into a multi-plate purifying column between its bottom space and still head, a diluting liquid consisting of one of the components of the liquid mixture is fed into the column, a distillate containing volatile impurities is obtained from the still head and the purified two-component liquid mixture is obtained from the bottom of the column, at least part of the heat contained in the distillate obtained from the still head is directed to the bottom space of the column, e.g. by passing the distillate through a heat exchanger transferring heat to the bottom space.



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METHOD AND APPARATUS FOR THE PURIFICATION OF A TWO-COMPONENT LIQUID MIXTURE BY DISTILLATION

The present invention concerns a method for the purification of a two-component liquid mixture by distillation, in which method the liquid mixture to be purified is supplied into a multi-plate purifying column, between its bottom space and still head, a diluting liquid consisting of one of the components of the liquid mixture is fed into the column, a distillate containing volatile impurities is obtained from the still head and the purified two-component liquid mixture is obtained from the bottom of the column.

The invention also concerns a distillation apparatus for the purification of a two-component liquid mixture by distillation, said apparatus comprising a multi-plate purifying column; feed equipment for supplying the mixture to be purified into the column below the top plate; feed equipment for supplying a diluting liquid consisting of one of the components of the liquid mixture into the column; a still head outlet, with possible refluxing, for the removal of the distillate vapours from the still head; and a bottom outlet, with possible refluxing, for the removal of the bottom product from the bottom of the column.

In particular, the invention relates to a method and an apparatus for the purification of a two-component liquid mixture by distillation, said two-component liquid mixture containing a compound with a higher boiling point and another compound with a lower boiling point. These compounds of the liquid mixture may be any liquids permitting purification by distillation. More particularly, the invention concerns a method and a corresponding apparatus for the purification of a mixture of water and ethanol in the manufacture of drinkable alcohol.

To produce drinkable alcohol from fermented

mash, the alcohol is usually separated by distillation in a mash column in which raw alcohol is obtained from the still head and the grain with low alcohol content from the bottom. Depending on the distillation system used, the raw alcohol obtained from the mash column, usually having an alcohol concentration of 30 - 50 % by weight, can be passed to a purifying or hydroselection column either directly in the vaporized state or in liquid state after condensation, or after it has been rectified into raw spirit, which typically has a concentration of 88 - 94 % by weight.

In the purifying column, the raw alcohol or raw spirit is diluted with water and subjected to extractive distillation. During this stage, the raw alcohol is effectively purified of substances that are undesirable in clear spirit of neutral smell and taste, e.g. vodka.

These undesirable impurities are typically amyl alcohols, aldehydes, esters and other organic compounds occurring in small quantities in raw alcohol. The evaporability of the impurities increases as the ethanol content of the water-ethanol mixture decreases. To achieve the required decrease of the ethanol content in the purifying column, water is supplied into it to dilute the raw alcohol or raw spirit during distillation. The dilution with water effects a large increase in the relative evaporability of undesirable compounds, causing the latter to concentrate in the still head, from where they can be removed as a so-called forerun. The purified and diluted alcoholic solution obtained from the bottom of the column is passed into a rectifying column where it is rectified anew. The rectified alcohol is obtained from the top of the rectifying column while the water with low alcohol content is obtained from the bottom and can be reused as diluting water in the purifying column. The rest of the impurities contained in the ethanol- water mixture

obtained from the bottom of the purifying column are concentrated partly in the still head and partly in the so-called fusel zone of the rectifying column, from where they can be removed. The fusel zone of the rectifying column is located in the region where the ethanol content of the ethanol-water mixture boiling on the column plates is approx. 10 - 70 % by weight.

If necessary, to improve the quality of the rectified distillation product obtained from the rectifying column, a so-called methanol column is used. From this, the pure alcohol is obtained from the bottom while the fraction containing impurities, e.g. methanol, is obtained from the still head.

In principle, industrial extractive purification of raw alcohol can be implemented in two ways regarding the manner in which the diluting water is supplied into the column. In one alternative, the raw alcohol and the required diluting water are fed in together onto the same plate, located several plates below the still head. The purified ethanol-water mixture, typically having a concentration of 8-20 % by weight, is obtained from the bottom of the column while the undesirable compounds are removed from the still head in the form of distillate vapour. Since the input plate or plates of the column are below the top plate, part of the ethanol-containing vapour obtained from the still head is returned after condensation back to the top plate to enable the top part of the column to function. Due to this refluxing, the ethanol content of the distillate vapour obtained from the still head typically amounts to a value exceeding 80 % by weight.

In the other alternative operational mode of a purifying column, the raw alcohol is fed into the column at a point below the top plate while the diluting water is supplied onto the top plate of the column. The purified ethanol-water mixture, typically having a concentration of 8-20 % by weight, is obtained from the

bottom of the column. The undesirable compounds are removed from the still head of the purifying column in the form of a distillate vapour which typically has an ethanol concentration below 30 % by weight. In this alternative, the distillate vapour obtained from the still head need not be refluxed after condensation back to the top plate, because the diluting water supplied to the top plate constitutes a reflux in the upper part of the column and is responsible for the low ethanol content of the distillate vapour obtained from the still head.

In the case of both of these solutions regarding the operation of the purifying column, the liquid is heated to a boiling temperature by means of steam either directly by supplying it into the bottom space of the column or indirectly using a heat exchanger. In both cases, the purifying column typically needs 1 - 3 MJ of external energy per 1 kg of purified ethanol (100%).

The object of the invention is to achieve a method and an apparatus for implementing purifiying distillation in such a way as to reduce the energy required for the distillation to a level essentially below the energy requirement of previously known methods and apparatuses.

The present invention provides a new and surprising solution regarding the energy requirement of the purifying column. Using the arrangement provided by the invention, the heat content of the vapour obtained from the still head of the purifying column can be utilized for the heating of the bottom space of the same column. According to the invention, the vapour obtained from the still head of the purifying column need not be compressed mechanically or by other means to increase its temperature.

In the purification of a two-component liquid mixture, either the mixture itself or one of its compo-

nents, e.g. the one with the lower boiling point, is fed into the purifying column at a point several plates below the top plate of the column. The other component, e.g. a diluting liquid having a higher boiling point, is supplied into the purifying column at a point above the point of supply of the component with a lower boiling point and/or onto the top plate of the column. The supply of the diluting liquid and the operational conditions in the column are adjusted as described below so as to ensure that the temperature in the still head is higher than the temperature at the bottom of the column. When this is the case, the vapour obtained from the still head can be used for the heating of the bottom space.

The apparatus of the invention comprises equipment for supplying a diluting liquid onto the top plate, below the top plate or both onto and below the top plate, and equipment for supplying the liquid mixture to be purified into the purifying column at a point below the point of supply of the diluting liquid. The novelty in the apparatus of the invention is its equipment for passing part of the heat content of the distillate vapour obtained from the still head into the bottom space of the column e.g. by means of a heat exchanger serving to maintain a boiling temperature in the bottom space.

In practice it was discovered that the temperature of the distillate vapour obtained from the top of the purifying column belonging to the purifying distillation system used in the production of drinkable alcohol was higher than the boiling point of the liquid in the bottom space. Upon closer investigation of the matter, it was discovered that the temperature of the distillate vapour obtained from the top of the purifying column and the temperature of the liquid boiling in the bottom space showed large variations depending on the operating conditions in the column. In the first opera-

tional mode of the purifying column, the boiling temperature of the liquid at the bottom was always distinctly higher than the temperature of the distillate vapour obtained from the top of the column because the liquid at the bottom has a lower ethanol content and a higher pressure than the distillate vapour obtained from the top. In the second operational mode of the purifying column, by varying the amount of diluting liquid used, the position of the point of supply of raw alcohol in the column and the intensity of the boiling, it is possible to exert a strong influence on the temperature of the distillate vapour removed from the top of the column and, to a lesser extent, on the boiling point of the liquid at the bottom of the column. When the diluting water is supplied onto the top plate of the column, the result is a decrease in the ethanol content of the liquid boiling on the plates in the upper part of the column, which again leads to an increase in the temperature of the distillate vapour removed from the top of the column. If the quantity of diluting water is sufficient, the temperature of the distillate vapour removed from the top of the column will rise above the boiling temperature of the liquid boiling in the bottom space of the column. This temperature difference is the larger the smaller is the pressure loss, i.e. the pressure difference between top and bottom of the purifying column.

In a typical case, the purifying column has 25 - 50 bubble, sieve or valve plates, across which the pressure loss in the column during distillation is usually 75 - 250 mbar. If packed column fillers with a small pressure loss are used, the pressure difference in the column can be kept at a level below 50 mbar.

By adjusting the distillation conditions in the purifying colum in such a way that the temperature of the distillate vapour removed from the purifying column is higher than the boiling point of liquid at

the bottom, it is possible to transfer the energy contained in the distillate vapour via a heat exchanger to the bottom of the same column for the boiling of the liquid, without compressing the vapour by mechanical or other means to produce a higher pressure or temperature.

In the method of the invention, the distillate vapour obtained from the still head of the purifying column is passed essentially as such and directly from the still head to the secondary side of a heat exchanger communicating with the bottom space of the same column, in such manner that the distillate vapour is partly or completely condensed in the exchanger, which transfers the condensation energy of the vapour to the bottom space for use in the boiling of the liquid.

The arrangement provided by the invention makes it possible to achieve a substantial reduction in the amount of external energy required by the purifying column.

The apparatus of the invention can also be used for the purifying distillation of raw alcohol or impure spirit produced in other ways besides fermentation, e.g. synthetic spirit.

When the method of the invention is used for the purification of alcohol, the alcohol to be purified has a concentration of e.g. 20 - 90 % by weight. In a typical case, the alcohol to be purified is raw alcohol obtained from a mash column and has a concentration of 35 - 50 % by weight. In another typical case, the alcohol to be purified is raw alcohol with a concentration of e.g. 88 - 94 % by weight.

The method and apparatus of the invention are also applicable for the purification of other liquid pairs besides water-ethanol mixtures. Such liquid pairs may consist e.g. of water and other kinds of alcohol, water and other organic liquids, and/or organic liquids in general.

In the following, the invention is described

in detail by the aid of examples of its embodiments, reference being made to the drawing attached, wherein:

Fig. 1 presents a flow chart illustrating the operation of an industrial-scale distillation apparatus representing the state of the art.

Fig. 2 presents a flow chart representing an embodiment of the method and apparatus of the invention.

Example 1:

In a distillery, a purifying column as illustrated by Fig. 1 was used. The column was a 45-plate bubble plate column.

Raw alcohol, e.g. the distillate obtained from a mash column, was supplied through feed line 2 into the middle region of the column. The raw alcohol feed can be preheated in some other heat exchanger belonging to the distillation system.

A sufficient amount of diluting water, preferably at a temperature close to that in the still head, e.g. the bottom product obtained from the bottom of a rectification column belonging to the distillation system, is supplied to the top plate of the purifying column via feed line 3.

The purified weak alcohol solution, typically having an ethanol content of 8 - 20 % by weight, was passed from the bottom space 6 via output line 7 to other parts of the distillation system for further processing.

The ethanol-containing vapour obtained from the still head 5 of the purifying column is passed via line 4 into a heat exchanger 12, where it is condensed. The condensed vapour, the so-called distillate, was removed from the heat exchanger via line 10 and directed to other parts of the distillation system for further processing.

In addition, the apparatus was provided with another heat exchanger 8 connected to the bottom space of the column. Via line 10, primary vapour was supplied

to the primary side of the heat exchanger. The condensed vapour, the so-called primary condensate, was removed from the heat exchanger via exhaust line 11 and passed to other parts of the distillation system for further processing. The heat energy released in the condensation of the primary vapour was transferred to the secondary side of the heat exchanger and further via line 9 to the bottom space of the purifying column, causing the liquid in the bottom space to boil.

A materials and energy balance as shown in Table 1, based on measurements, was drawn up for the purifying column illustrated by Fig. 1.

The materials balance revealed that during practical distillation the temperature of the ethanol-containing vapour (flow line 4) obtained from the still head was higher than the boiling point in the bottom space (flow line 7) of the same column, and that, by using a heat exchanger, the heat energy of the ethanol-containing vapour could be utilized for maintaining a boiling temperature in the bottom space of the column.

Table 1: Materials and energy balance

Flow	In EtOH kg/h	In tot. kg/h	Out EtOH kg/h	Out tot. kg/h	Ent. +/- MJ/h
2. Raw alcohol feed 1288 mbar, 60°C	1556	2961			+589
3. Diluting water feed 1204 mbar, 104°C	0	11000			+4795
4. Distillate vapour 1204 mbar, 105°C			29	1098	-2909
7. Bottom product 1364 mbar, 99.1°C			1527	12863	-5102
10. Vapour 2 bar, 120°C	0	1193			+3228
11. Primary condensate 2 bar, 120°C			0	1193	-601
Sum of column	**1566**	**15154**	**1556**	**15154**	**0**

Abbreviations:
EtOH = ethanol mass flow
tot. = total mass flow
ent. = flow enthalpy; liquid at 0°C temperature reference level in enthalpy calculation
\+ = direction of enthalpy flow inward from outside the balance limit
\- = direction of enthalpy flow outward from within the balance limit

Example 2:

From the materials and energy balance presented in Table 1, the thermal power fed into heat exchanger 8 in example 1 can be calculated as follows:

+ 32238 MJ/h - 601 MJ/h = 2627 MJ/h
(flow 10) (flow 11)

It can be shown by calculations that the distillate vapour flow 4 in example 1 is condensed under 1204-mbar pressure as follows:

1098 kg/h ----->	1098 kg/h	+ 2427 MJ/h
distillate vapour	condensate	condensation heat
1204 mbar, 105°C	1204 mbar, 101.9°C	

Since the distillate vapour flow 4 has an ethanol content of 2.64 % by weight, the temperature falls in the total condensation from 105°C to 101.9°C. Since the condensation temperature in the total condensation is higher than the temperature in the bottom space of the purifying column in example 1, the distillate vapour can be directed to a heat exchanger providing heat for the boiling of the liquid in the bottom space as illustrated by Fig. 2, thus enabling the entire condensation heat to be transferred to the bottom space to maintain the boiling temperature.

To maintain a thermal balance in the column, it is necessary to supply the column with primary boiling energy in the manner shown in Fig. 2, via heat exchanger 8b. The amount of energy required is as follows:

2627 MJ/h	-2427 MJ/h	= 200 MJ/h
boiling power of the heat	condensation	

vapour flow (4)

Example 2 shows that the method and apparatus of the invention enable the required external boiling energy of the purifying column to be reduced from a value of 2627 MJ/h to a value of 200 MJ/h.

The examples presented above only serve to illustrate the invention, and the embodiments of the invention may vary in the scope of the following claims.

CLAIMS

1. Method for the purification of a two-component liquid mixture by distillation, in which method the liquid mixture to be purified is fed into a multi-plate purifying column between its bottom space and still head, a diluting liquid consisting of one of the components of the liquid mixture is fed into the column, a distillate containing volatile impurities is obtained from the still head and the purified two-component liquid mixture is obtained from the bottom of the column, c h a r a c t e r i z e d in that at least part of the heat contained in the distillate obtained from the still head is directed to the bottom space of the column, e.g. by passing the distillate through a heat exchanger transferring heat to the bottom space.

2. Method according to claim 1, c h a r a c t e r i z e d in that the temperature of the distillate obtained from the still head is higher than the temperature in the bottom space of the column.

3. Method according to claim 1 or 2, c h a r a c t e r i z e d in that a diluting liquid consisting of one of the components of the two-component liquid mixture is fed into the column at a point located above the point of input of the mixture to be purified.

4. Method according to any one of claims 1 - 3, c h a r a c t e r i z e d in that a diluting liquid consisting of one of the components of the two-component liquid mixture is fed to the top plate of the column.

5. Method according to any one of claims 1 - 4, c h a r a c t e r i z e d in that the mixture to be purified is a mixture of ethanol and water.

6. Method according to claim 5, c h a r a c t e r i z e d in that the ethanol content of the ethanol-water mixture is 20 - 95 % by weight.

7. Method according to claims 3 and 4,

c h a r a c t e r i z e d in that the ethanol content of the vapour obtained from the still head is below 30 % by weight.

8. Distillation apparatus for the purification of a two-component liquid mixture by distillation, said apparatus comprising a multi-plate purifying column (1); feed equipment (2) for supplying the mixture to be purified into the column below the top plate; feed equipment (3) for supplying a diluting liquid consisting of one of the components of the liquid mixture into the column; a still head outlet (4) for the removal of the distillate vapours from the still head (5); and a bottom outlet (7) for the removal of the bottom product from the bottom of the column; c h a r a c t e r i z e d in that the apparatus is provided with a heat exchanger (8) and that the distillate vapours removed from the still head (5) are directed into the heat exchanger (8), which transfers at least part of the heat contained in the vapours into the bottom space of the column (1).

9. Method according to claim 8, c h a r a c t e r i z e d in that the diluting liquid is supplied to the top plate of the column by the relevant feed equipment (3), while the liquid mixture is supplied to a plate below the top plate of the column by the relevant feed equipment (2).

10. Apparatus according to claim 8, c h a r a c t e r i z e d in that it is provided with a heat exchanger (8b) for supplying the bottom space of the purifying column (1) with the thermal power needed for the starting-up of the column as well as the thermal power needed to maintain a thermal balance in the column during operation.

AMENDED CLAIMS
[received by the International Bureau
on 30 May 1990 (30.05.90);
original claims 1-10 replaced by amended claims 1-8 (2 pages)]

1. Method for the purification of a two-component liquid mixture by distillation, in which method the liquid mixture to be purified is fed into a multi-plate purifying column between its bottom space and still head, a diluting liquid consisting of one of the components of the liquid mixture is fed into the column, a distillate containing volatile impurities is obtained from the still head and the purified two-component liquid mixture is obtained from the bottom of the column, c h a r a c t e r i z e d in that the mixture to be purified is a mixture of ethanol and water, wherein the ethanol content is 20 - 95 % by weight; and that at least part of the heat contained in the distillate obtained from the still head is directed to the bottom space of the column, e.g. by passing the distillate through a heat exchanger transferring heat to the bottom space.

2. Method according to claim 1, c h a r a c t e r i z e d in that the temperature of the distillate obtained from the still head is higher than the temperature in the bottom space of the column.

3. Method according to claim 1 or 2, c h a r a c t e r i z e d in that a diluting liquid consisting of one of the components of the two-component liquid mixture is fed into the column at a point located above the point of input of the mixture to be purified.

4. Method according to any one of claims 1 - 3, c h a r a c t e r i z e d in that a diluting liquid consisting of one of the components of the two-component liquid mixture is fed to the top plate of the column.

5. Method according to claim 3 or 4, c h a r a c t e r i z e d in that the ethanol content of the vapour obtained from the still head is below 30 % by weight.

6. Distillation apparatus for the purification

of a two-component liquid mixture by distillation, said apparatus comprising a multi-plate purifying column (1); feed equipment (2) for supplying the mixture to be purified into the column below the top plate; feed equipment (3) for supplying a diluting liquid consisting of one of the components of the liquid mixture into the column; a still head outlet (4) for the removal of the distillate vapours from the still head (5); and a bottom outlet (7) for the removal of the bottom product from the bottom of the column; c h a r a c t e r i z e d in that the apparatus is provided with a heat exchanger (8) and that the distillate vapours removed from the still head (5) are directed into the heat exchanger (8), which transfers at least part of the heat contained in the vapours into the bottom space of the column (1).

7. Method according to claim 6, c h a r a c t e r i z e d in that the diluting liquid is supplied to the top plate of the column by the relevant feed equipment (3), while the liquid mixture is supplied to a plate below the top plate of the column by the relevant feed equipment (2).

8. Apparatus according to claim 6, c h a r a c t e r i z e d in that it is provided with a heat exchanger (8b) for supplying the bottom space of the purifying column (1) with the thermal power needed for the starting-up of the column as well as the thermal power needed to maintain a thermal balance in the column during operation.

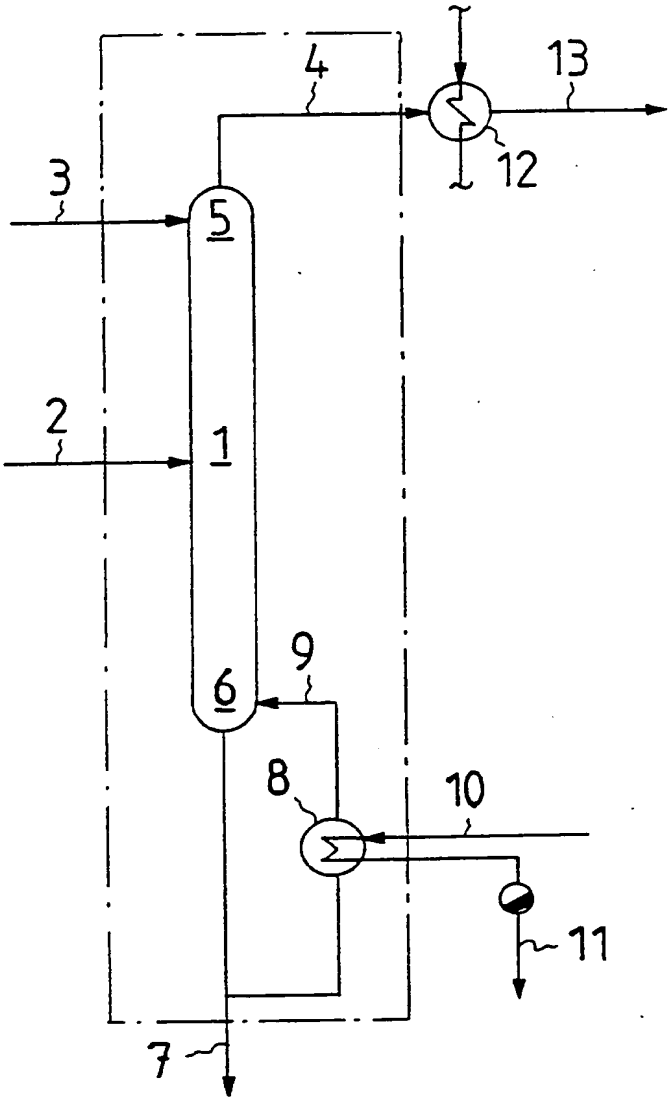

Fig.1

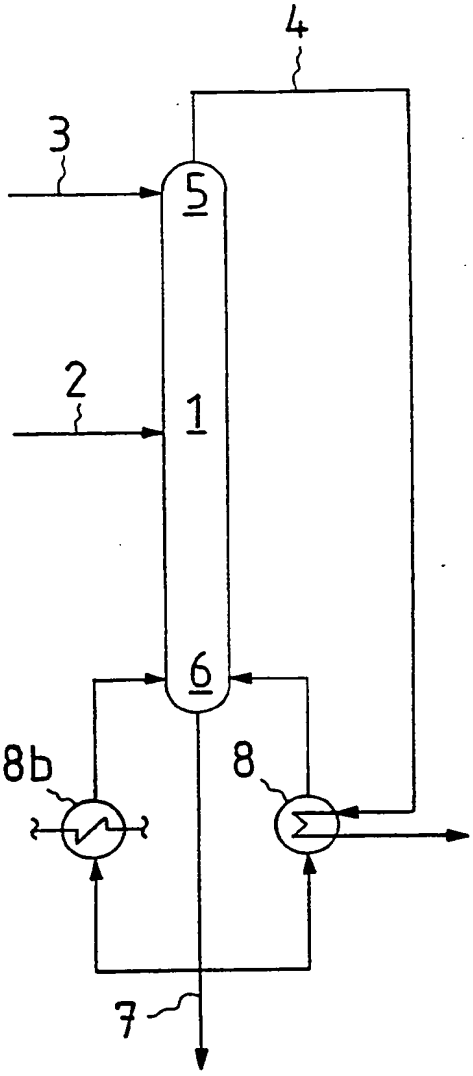

Fig.2

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI 90/00002

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: B 01 D 3/40, 3/18, C 12 F 1/04

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System [8]	Classification Symbols
IPC5	B 01 D; C 12 F; C 12 G

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [9]

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	SE, 193714 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V.) 5 January 1965, see page 2, column 1, line 30 - line 33; page 4, column 1, line 43; page 5, column 1, line 7 - line 8; page 5, column 1, line 41 - line 42; figure 1	1,3,4,8, 9
Y	--	5
X	SE, 193713 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V.) 5 January 1965, see page 1, column 1, line 28 - line 33; page 3, column 2, line 14 - line 16; page 4, column 1, line 22 - line 23; figure 1	1,3,4,8, 9
Y	--	5

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
29th March 1990	1990 -04- 05
International Searching Authority	**Signature of Authorized Officer**
SWEDISH PATENT OFFICE	Bengt Christensson

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	SE, B, 361824 (TREADWELL CORPORATION) 19 November 1973, see page 10, line 7 --	5
A	EP, A1, 0043023 (RAPHAEL KATZEN ASSOCIATES INTERNATIONAL, INC.) 6 January 1982, see page 10, line 35; abstract; claim 9 --	1,5-8
A	SE, B, 451846 (NAUCHNO PROIZVODSTVENNOE GIDROLIZNOE OBIEDINENIE) 2 November 1987, see page 6, line 13 - line 16; figure 1 --	1-4,8-9
A	DE, A1, 2340566 (PETER, SIEGFRIED) 27 February 1975, see figures 1-2 --	1-4,8-9
A	EP, A2, 0203259 (LINDE AKTIENGESELLSCHAFT) 3 December 1986, see page 2, line 9 - line 15; page 5, line 10 - line 12; figures 1-2 --	1-4,8-9

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/FI 90/00002

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
SE- - 193714	65-01-05	NONE		
SE- - 193713	65-01-05	NONE		
SE-B- 361824	73-11-19	BE-A-	730474	69-09-01
		CH-A-	487662	70-03-31
		DE-A-	1915437	69-11-13
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		GB-A-	1250236	71-10-20
		NL-A-	6904660	69-09-30
		US-A-	3575007	71-04-13
EP-A1- 0043023	82-01-06	AU-B-	540240	84-11-08
		AU-D-	7063681	82-01-07
		CA-A-	1173400	84-08-28
		US-A-	4306942	81-12-22
SE-B- 451846	87-11-02	AU-D-	9128482	83-04-08
		CH-A-B-	657149	86-08-15
		DE-T-	3249029	86-06-19
		DE-C-	3249803	87-07-16
		GB-A-B-	2117259	83-10-12
		SE-A-	8302872	83-05-20
		WO-A-	83/01070	83-03-31
DE-A1- 2340566	75-02-27	CH-A-	602152	78-07-31
		GB-A-	1474207	77-05-18
		NL-A-	7410319	75-02-12
		US-A-	4345976	82-08-24
EP-A2- 0203259	86-12-03	DE-A-	3504032	86-08-07
		US-A-	4670027	87-06-02